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(54) Title: PREPARATION OF CORE-SHELL POLYMER PARTICLES CONTAINING VOIDS			
(57) Abstract			
<p>The invention relates to a process for making core-shell polymer particles containing voids which comprises first emulsion polymerization of a core from a core monomer system comprised of at least one unsaturated monomer containing acid functionality optionally in the presence of seed latex, then encapsulating said core with a hard shell by emulsion polymerizing a shell monomer system containing at least a vinyl aromatic or/and unsaturated carboxylic ester in the presence of said core, and finally swelling at elevated temperature the resultant core-shell polymer particles with volatile base, shell monomers, a radical inhibitor and a non-ionic surfactant followed by polymerization of shell monomers charged at swelling stage to produce an aqueous dispersion of particles which, when dried contain a microvoid which causes opacity in compositions. The core-shell particles produced by the process described above are used in opaque and glossy coatings.</p>			

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Preparation of Core-Shell Polymer Particles Containing Voids

5 Field of the Invention

The present invention relates to a process for preparing with core-shell particles containing microvoids by emulsion polymerization. More specifically, the present invention relates to a process for preparing emulsion polymers which comprise an internal layer with an alkali-
10 swellable resin, carrying out a subsequential emulsion polymerization to form a hard polymer layer outside the internal layer, swelling the internal layer with an alkali or more exact volatile base such as ammonia or amine and then drying to remove water contained in the alkali-swellable resin, thereby forming a microvoid in the center of polymer particle. Polymer particles containing voids are useful as opacifying agents in coating applications
15 such as paint or paper coating, particularly for high quality paper products where colour pictures are presented, such as art books, brochures, magazines etc. The use of microvoid containing polymer particles reduces or removes the need for inorganic pigments, such as titanium dioxide, or extenders, without adding excessive and undesirable weight to coating. Microvoid containing polymer particles have found extensive applications as white plastic
20 pigments and they have started to replace the earlier used polymers filled uniformly in particles.

Description of the Prior Art

25 In the prior art a number of methods for the production of polymer particles containing microvoids have been known. Some methods have been proposed without application of core-shell particles as precursors of microvoid containing polymer particles. US 4 973 670 discloses a process for preparing polymer particles containing microvoids by a two step emulsion polymerization. The first step involves introducing of an organic phase to an
30 aqueous phase. The organic phase comprises monomer which is insoluble in the aqueous phase and water insoluble hydrocarbon. The monomer is polymerized to produce a low molecular weight polymer such that the polymer will phase separate from organic phase and concentrates at the surface of the introduced organic phase. The second step is an additional polymerization of a crosslinking monomer with the low molecular weight

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polymer to produce microvoid containing particles. The main drawback of the process is a necessity to remove the hydrocarbon by stripping.

US 5 360 827 discloses a process for preparation of polymer particles containing microvoids which are prepared by adding a base in the presence of a monomer to a latex
5 containing copolymer particles modified carboxylic to make the pH of the latex 8 or more, and by adding monomers containing carboxyl group to make pH of the latex 7 or less and then by polymerizing these monomers. This process leaves high amounts of residual monomers in the product and thus an additional steam distillation operation is required. Besides, a structure of the particles prepared is rather indefinite. As a rule each particle
10 contains several voids.

US 5 578 650 discloses a process for emulsification of (meth)acrylate ester in the presence of water and at least one acid that is not free radically polymerizable and an emulsifier followed by (meth)acrylic ester polymerization to produce microspheres, a majority of which have cavities that upon drying become voids. Similar to the process according to US
15 5 360 827 each particle contains as a rule several voids. Moreover particles are too high in size to provide good opacifying ability.

A number of processes for making polymer particles containing microvoids based on an application of core-shell particles as precursors of the polymer particles are known. These processes provide a preparation of polymer particles containing microvoid of more definite
20 structure, namely a single microvoid in the center of a polymer particle. In addition said processes have suitable particle size, usually 0.1-2.0 mm. for opacifying.

US 4 427 836 discloses a process for making core-shell polymer particles containing microvoids, comprising (A) emulsion polymerization a core from a core monomer system comprised at least one ethylenically unsaturated acid monomer; (B) encapsulating said core
25 with a hard shell by emulsion polymerization a shell monomer system in the presence of said core; (C) neutralizing with ammonia or amine so as to swell said core and form particles which, when dried, contain a single void. According to the process at least one additional shell can be polymerized subsequent to step (C). However, the process has several disadvantages. The first one is in that the stability of latex is poor, particularly at
30 stage (A) due to polarity and hydrophilicity of highly carboxylated core and low adsorption energy of a surfactant. That is why a lot of coagulate is formed during this stage. The second disadvantage consists in that the conditions of particle swelling and their expansion are not suitable enough particularly when glass transition temperature (T_g) of a shell

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polymer is higher than 100°C. e.g. Tg of poly(methyl methacrylate) is 105°C. According to examples of US patent No. 4,427,836 temperature of neutralization does not exceed 95°C. The situation with the conditions of particle swelling can be improved. US 4 594 363 discloses a process for making core-shell polymer particles containing voids comprising
5 emulsion polymerizing a core from a core monomer system comprised of at least one ethylenically unsaturated monomer containing acid functionally encapsulating said core with a hard sheath by emulsion polymerizing a shell monomer system in the presence of said core and swelling at elevated temperature the resultant core-shell polymer particles with fixed or permanent base in the presence of solvent. Naturally the solvent decreases Tg
10 of the shell polymer and alleviates the swelling. The main drawback of the process is a presence of organic solvent in the final polymer dispersion. Besides, the problems with the latex stability during highly carboxylated core preparation remain to be solved.

The processes disclosed in US 4 970 241 and US 5 157 084 are free of these disadvantages due to a core polymer does not contain acid monomer units or contains a small amount. US
15 4 970 241 discloses multi-stage polymer particles containing one or more void space(s) which are produced by sequential emulsion polymerization of an essentially low-acid earlier polymer stage, encapsulation of said low-acid polymer stage with at least a final polymer stage, contacting said polymer particles with a non-polymeric carboxylic acid or anhydride to be absorbed into said low-acid polymer stage and swelling the polymer
20 particles by contacting the particles with an aqueous base at a temperature near or above the Tg of the polymer. The non-polymeric acid or anhydride plasticize the polymer. Thus a temperature of swelling stage can be reduced. The main drawback of the final product is a presence in a polymer dispersion of rather large amount of low molecular weight salt of organic acid.

25 US 5 157 084 discloses a process of making polymer particles containing microvoids also without the use of acid in the swellable polymer core. A swellability of the polymer core at elevated temperature is achieved by incorporation into the core polymer (meth)acrylate ester units which are hydrolyzable in alkaline environments. The drawback of the process is too high temperature of the hydrolysis process (up to 150°C). Thus the process must be
30 performed under pressure. Besides usually problems with latex stability arise at such severe conditions. One more drawback is that before the hydrolysis the core is to be encapsulated with two shells. In other words an intermediate shell is necessary to provide

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complete encapsulation of the core. This adds complexity to the process.

It should be noted that the majority of the known processes comprises the stage of an intermediate shell preparation. This stage is obligatory when the hard outer shell is obtained on the basis of hydrophobic monomers such as styrene, α -methyl styrene, vinyl toluene etc. Nevertheless US 5 494 971 contemplates a hydrophilic core can be encapsulated with hydrophobic shell without intermediate shell or tie coat.

What actually happens is that according to said US patent the acid functional monoethylenically unsaturated monomer is added during the polymerization of the shell polymer over the first 50% of the total shell monomer feed or more depending on the particle size of the core. Thus the hydrophilicity of the shell is gradually altered from the inner layer to the outer layer. In other words tie coat is present although its hydrophilic properties are changed along the particle radius. Approximately the same approach is disclosed in patent application WO 95/11265 when a continuous variation in composition of shell monomer system takes place in order to realize gradual transition from a hydrophilic core to a hydrophobic outer layer of the shell.

Both of the mentioned processes are rather complicated due to a specific program for shell monomer system feed and additional equipment are required. In general all of the said methods of the state of art are multistage processes, at least three-stage ones when polarities of a core and a shell monomer systems are comparatively close. When the shell is prepared on the basis of cheaper hydrophobic monomers such as styrene at least one more stage, namely intermediate shell preparation, is necessary. Besides there are some problems with latex stability due to high hydrophilicity of core polymer or high temperature of particle swelling. Moreover conditions of the swelling are not always adequate. Either a temperature of the swelling process is too low compared to T_g of the shell polymer or a final product contains unnecessary admixtures charged during the swelling process to plasticize the shell polymer.

Summary of the Invention

It is therefore an object of the present invention to provide an improved production of emulsion core-shell opacifying polymers containing a hydrophilic core polymer fully encapsulated with a hard shell polymer preferably without the use of an intermediate shell even if the hard shell consists of hydrophobic units of a cheaper monomer such as styrene.

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It is another object of the present invention to provide an improved process with reduced coagulate formation during the emulsion polymerization particularly at the stage of hydrophilic highly carboxylated core preparation. It is still another object of the present invention to provide an increase of opacifying ability of the final product by an improvement of the swelling procedure so that said final product does not contain unnecessary low molecular weight admixtures.

These objects which will become apparent from the following disclosure are achieved by the present invention which comprises a process for making core-shell polymer particles containing voids, said particles useful for opacifying, comprising (A) emulsion polymerization a core from a core monomer system comprised of ethylenically unsaturated monomer containing acid functionality; (B) encapsulating said core with a hard shell by emulsion polymerizing a shell monomer system in the presence of said core, and (C) swelling at elevated temperature the resultant core-shell polymer particles with volatile base so as to produce an aqueous dispersion of particles which when dried contain a microvoid which causes opacity in compositions in which they are contained, characterized in that

(1) core monomer system comprises from about 50.0% by weight to about 79.9% by weight, based on the total weight of the core monomer system, of (meth)acrylic ester from about 20.0% by weight to about 40% by weight, based on the total weight of the core monomer system unsaturated carboxylic acid, from about 0.1% by weight to about 1.0% by weight, based on the total weight of the core monomer system, and optionally from about 5% by weight to 15% weight, based on the total weight of the core monomer system of crosslinking monomer, of vinyl aromatic monomer;

(2) before stage (C) from 1.0 by weight to 40% by weight, based on the total weight of the core-shell particles, of the shell monomers; from 0.01 by weight to 0.40% by weight, based on the total weight of the core-shell particles, of a radical inhibitor and from 0.02% by weight to 1.2% by weight, based on the total weight of the core-shell particles are charged into the dispersion of the core-shell particles;

(3) stage (C) carried out at the temperature higher than glass transition temperature of the system of shell polymer-shell monomers added at stage (C) is followed by (D) polymerization of shell monomers charged at stage (C).

(4) Stages (A) and (B) are carried out at continuous feeding of all of the components as two flows, the first one comprising the monomer mixture and the second one comprising the

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aqueous solution of initiator and surfactant. In another aspect, the invention comprises latex compositions comprising core-shell polymer particles prepared by the said process and coatings which are produced with the compositions.

5 Detailed Description of the Invention

All polymerization stages of the process are carried out as semi-continuous emulsion polymerization stages. Emulsion polymerization is carried out in the presence of water-soluble free radical initiators such as sodium, potassium or ammonium persulphate and
10 anionic surfactants such as sodium dodecyl benzene sulphonate, sodium alkyl sulphonate, sodium lauryl sulphate at a temperature from 70°C to 95°C. Semicontinuous polymerizations are carried out at continuous feeding of the components. This approach has a number of advantages.

1. A constant feeding of an initiator provides high rate of polymerization so that "monomer
15 starvation" conditions are realized and a kinetic steric barrier is arisen. It means correct core-shell morphology is formed without any phase inversion even if hard hydrophobic shell is formed onto hydrophilic core.

2. A constant feeding of a surfactant allows to carry out polymerization onto seed particles only, i.e. without formation of new particles. It's very important particularly for stage (B)
20 because formation of new particles at this stage means the occurrence of the particles free of carboxylated core which are not able to swell in the presence of base at stage (C).

A constant feeding of all of the components reduces a coagulate formation during the polymerization.

The core polymer is the product of aqueous emulsion copolymerization of (meth)acrylic
25 ester, unsaturated carboxylic acid, cross-linking monomer and optionally vinyl aromatic monomer. Suitable (meth)acrylic esters include methyl methacrylate, ethyl methacrylate, butyl(meth)acrylate, 2-ethylhexyl (meth)acrylate. Suitable unsaturated carboxylic acids include acrylic acid and methacrylic acid, which are preferred, and itaconic acid, maleic acid or anhydride and monomethyl maleate or monomethyl itaconate. The cross-linking
30 monomer is meant to include monomers conventionally known in the art as useful for preparation of crosslinked polymers. Examples of such monomers typically include di- and trifunctional monomers having two or three unsaturated bonds such as divinyl benzene,

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ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,1,1-trimethylol propane trimethacrylate and allyl methacrylate. Vinyl aromatic compounds, such as styrene, p-methylstyrene and mixtures of isomers of methylstyrene can optionally be used.

In the copolymerization of core polymer 49.9-79.9 weight parts, preferably 59.5-74.5 weight parts of (meth)acrylic ester and 20-35 weight parts, preferably 25-30 weight parts of unsaturated carboxylic acid, and 0.1-1.0 weight parts, preferably 0.4-0.6 weight parts of crosslinking monomer, and optionally 0-15 weight parts, preferably 0-10 weight parts of vinyl aromatic monomer are used.

The acid-containing core polymer may be obtained also by a process involving a stage of seed latex preparation. The seed latex is prepared by emulsion copolymerization of 96.0-99.5 weight parts, preferably 97.0-98.5 weight parts of (meth)acrylic esters with 0.5-4.0 weight parts, preferably 1.5-3.0 weight parts of unsaturated carboxylic acid as a batch process. The amounts of components at seed step are as follows: 100 weight parts of distilled water, 1.0-4.0 weight parts, preferably 2.0-3.0 weight parts of monomers, 0.04-0.5 weight parts, preferably 0.1-0.3 weight parts of initiator and 0.001-0.040 weight parts, preferably 0.005-0.015 weight parts of anionic surfactant. The seed particles may have an average size in the range of 70 to 100 nm diameter.

It is very important to find correct amounts of the seed latex and the other components at the final stage of the highly carboxylated core polymer preparation, which is carried out straightaway after the completion of the seed step. These amounts are as follows: 1.0-4.0 parts by weight solids, preferably 2.0-3.0 parts by weight solids of the seed latex, 10-70 weight parts, preferably 20-40 weight parts of the monomer mixture comprising (meth)acrylic ester, unsaturated carboxylic acid and crosslinking monomer and vinyl aromatic monomer, 0.03-0.6 weight parts, preferably 0.10-0.30 weight parts of the anionic surfactant and 0.05-0.50 weight parts, preferably 0.10-0.25 weight parts of the initiator.

Said ratios of the components provide a stable core polymer latex preparation with low content of coagulate (less than 3.5 wt-%). Average particle size depending on the selected ratio of the components is in the range of 140 to 320 nm. More preferable average particle size is from 200 nm to 220 nm. The core polymer latex is unsaturated one with a surfactant due to surface tension is in the range of 39 to 50 mN/m. Hence a correct choice of the surfactant concentration at stage (B) excludes a formation of new particles.

Surprisingly the present inventors have found that incorporation of vinyl aromatic monomer units into the core polymer provides the preparation of core polymer latex

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completely free of coagulate.

After the acid core is obtained, a subsequent stage of emulsion polymerization is effected to form a shell polymer on the acid core polymer particles. This may be performed in the same reaction vessel in which the formation of the core was accomplished or the reaction medium containing the dispersed core particles may be transferred to another reaction container.

The shell monomer system comprises vinyl aromatic monomer and/or (meth)acrylic esters. The shell monomer system may or may not contain a small amount of acid component (no more than 3.0% by the weight of the total amount of the shell monomers). The shell monomer system may or may not contain a crosslinking monomer.

Stage (B) may or may not comprise two or more steps with various monomer compositions.

At stage (B) 0.3-4.0 weight parts based on 100 weight parts of the shell monomers, preferably 0.8-2.0 weight parts of initiator and 0.1-1.5 weight parts based on 100 weight parts of the shell monomers, preferably 0.4-0.8 weight parts of surfactant are used. These amounts and feeding of components provide high rate of polymerization (monomer starvation conditions) and permit to avoid the occurrence of new particles. The diameter of core-shell particles is in the range from 250 to 800 nm.

The weight ratio of core polymer to shell polymer is from 1:4 to 1:40, preferably from 1:6 to 1:20. Swelling of the core-shell particles at stage (C) with volatile base are to be carried out at a temperature higher compared to T_g of shell polymer. Under such kind of conditions only one may expect an adequate swelling and expansion of the particles. As a rule T_g of the hard shell polymer is above 100°C. That is why even an application of elevated temperatures (85-95°C) at stage (C) is not enough. In order to reduce T_g stage (C) is performed in the presence of a monomer or monomer mixture. To prevent polymerization of the monomers charged at stage (C) a radical inhibitor is added simultaneously. When the swelling of the particles is completed an additional amount of initiator is charged into the reaction system and added monomers are polymerized. Thus the final polymer dispersion does not contain any organic low molecular weight admixtures. US 4 594 363 indicates that the swelling can be carried out in the presence of the shell monomer system. However there are not any examples in the patent descriptions. Besides comparative examples have shown that the swelling of the particles is not effective

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enough when the radical inhibitor is absent due to monomers added at stage (C) are polymerized quickly at elevated temperature. Thus opacifying of the final product is much lower compared to the product prepared according to the procedure disclosed in the present invention.

- 5 The monomers at stage (C) can be added before, after, or with the addition of the volatile base.

Before the swelling to prevent a partial coagulation of the polymer dispersion a nonionic surfactant is added. Usually the shell monomer system is applied at stage (C) as a component Tg reducing. However other monomers compatible with core-shell polymer can
10 be used, e.g. crosslinking monomers to increase Tg and hardness of the final product. Suitable amounts of the monomers added at stage (C) are about 1-40 parts by weight, based on 100 parts by weight core-shell polymer, preferably 5-15 parts by weight.

K.Adachi et al. in their study published in J.Polymer Sci., Polymer Phys.Ed., v.13, No. 11, p. 2155-2171 (1975) show that addition from 5 to 10 weight parts of low molecular weight
15 organic solvent per 100 weight parts of polystyrene reduces Tg up to 60-80°C.

Suitable radical inhibitors are well-known effective acceptors of free radicals such as benzoquinone, hydroquinone, nitrobenzene, trinitrobenzene, stable radicals such as diphenylpicryl hydrozyl, nitroxyl radicals etc.

The amount of the radical inhibitor depending on the amounts of the monomers added at
20 stage (C) is in the range from 0.01 to 0.40 parts by weight, based on 100 parts by weight core-shell polymer, preferably 0.05-0.15 parts by weight.

Nonionic surfactant, such as ethoxylated aliphatic alcohol or alkyl phenol depending on the amounts of the monomers added at stage (C) is used in amounts of 0.02 to 1.2 parts by weight, based on 100 parts by weight core-shell polymer, preferably 0.1-0.5 parts by
25 weight.

Volatile bases, such as ammonia or volatile organic bases, such as trimethyl amine, triethyl amine or diethyl ethanol amine are used as suitable swelling agents in amounts of 1.0-1.5 equivalents per 1 equivalent of carboxy-groups incorporated into the core-shell polymer.

Due to elevated temperature (85-95°C) at the swelling procedure the stage (C) is carried
30 out in the closed reactor under a small pressure (no more than 0.5 kg/cm²) in order to prevent a volatile base loss because non-controlled loss of the volatile base deteriorates the process reproducibility.

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When the swelling procedure is completed an additional amount of initiator (0.5-1.0 parts by weight, based on 100 parts by weight monomers added at stage (C)) is charged to polymerize said monomers (stage D).

An optional stage (E) comprises preparation of an additional shell with elevated T_g or vice versa with reduced T_g to prepare film forming polymer dispersion. For this stage vinyl aromatic monomers and/or (meth)acrylic esters are used. Crosslinking monomers may or may not be used. The conditions of stage (E) are practically the same as those at stage (B). The resulting polymer dispersions obtained according to the present invention depending on the ratios of the components and the reaction conditions have the following properties:

10 - solids 25-40 wt-%

- pH 7-9

- surface tension 40-55 mN/m

- particle size observed by means of a transmission electron microscope 500-950 nm

- residual monomers - less than 0.05 wt-%.

15 The multistage core-shell polymer dispersions of the present invention are useful for aqueous coating compositions as opacifying agents either as a supplement to, or replacement of, pigmentary matter and/or extenders therefore. For these purposes, the aqueous dispersions of the core-shell polymer may be added directly to the waterborn coating compositions. Surprisingly the present inventors have found that the gloss of the
20 coatings prepared on the basis of said coating compositions can be controlled by the composition of the core polymer. It turns out when the core polymer contains vinyl aromatic monomer units the coatings prepared are glossy. When the core polymer is free of vinyl aromatic units the coatings prepared are nonglossy or mat.

The opacifying ability of the core-shell polymer particles containing voids obtained
25 according to the present invention is defined as a contrast ratio of the coatings prepared with a film forming polymer dispersion and said core-shell polymer particles. The contrast ratio is determined by photometric method. 4 to 5 glass plates are coated with a coating composition (film forming latex of styrene-n-butyl acrylate-methacrylic acid 37:58:5 wt-% + said core-shell polymer dispersion). The reflection coefficient of the coated glass plate at
30 $\lambda=582$ nm is determined using a photometer. The glass plate is placed on a white surface with reflection coefficient of 86% and then on black surface with reflection coefficient of less than 1%. The contrast ratio R is calculated as the ratio of reflection coefficients. Then

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a linear dependence of R versus a reciprocal value of the weight content of core-shell polymer for a surface of 1 m² (1/w) is constructed. For evaluation of opacifying ability of the core-shell polymer particles containing voids R at w= 40g/m² is calculated on the basis of the mentioned dependence. Gloss of the coatings is determined as a reflection
5 coefficient at the incident ray angle of 45°.

Examples

10

The present invention is more specifically explained by the following examples. However, it should be understood that the present invention is not limited to those examples in any manner.

15 Example 1

Preparation of core polymer with varied ratios of monomers (Stage A)

The process is carried out in 250 ml flask equipped with stirrer, reflux condenser, inlet for
20 nitrogen and necks for feeding components. The feed is fulfilled with syringe pumps.

Step 1. Seed latex preparation

Recipe of monomer mixture 1:

Methyl methacrylate (MMA) 0.544 g

25 n-Butyl acrylate (BA) 0.650 g

Methacrylic acid (MAA) 0.056 g

Sodium dodecylbenzene sulphonate (SDBS) 3.00 g

(as 0.21% aqueous solution)

Potassium persulphate (PP) (as 1.96% aqueous solution) 6.12 g

30 Distilled water 45.0 g

This step is carried out as a batch process. 45.0 g of distilled water is charged into the flask

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and heated up to 82°C with stirring and nitrogen flow. Then SDBS solution is charged. In 5 min. PP solution and monomer mixture 1 are added. The process period (after the monomer mixture charge) is 1 hour.

Average particle size of seed particles is 90 nm.

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Step 2. Final acid containing core polymer preparation

Recipe:

Seed latex prepared at step 1

10 Monomer mixture 2 (composition is varied, see table 1) 33.00 g

SDBS (20.8% aqueous solution), amount varied, see table 1

PP 0.166 g

Distilled water 96.00 g

15 Step 2 starts straight away after completing step 1. The monomer mixture 2 and aqueous phase are simultaneously fed into the seed latex within 3 hours. Then the process continues for another 20 min. followed by cooling, discharging and filtering of the latex prepared. The properties of the latexes prepared depending on the monomer mixture 2 composition and SDBS amount are listed in table 1.

20

Table 1: Properties of core polymer latexes

Examp- le No wt-%	SDBS as 20.8% wt-%		Monomer mixture 2 amount/wt-%				Particle size, nm	Solids.	Surface wt-%.	Coagulate, tension, mN/m
	solution g	based on core polymer	MMA	ST	MAA	EGDM				
25										
1A	0.27	0.17	69.64	29.85	0.51		210	18.4	49.0	9.1
1B	1.35	0.85	69.64	29.85	0.51		200	19.7	44.0	4.4
30	1C	1.68	69.64	29.85	0.51		175	18.2	41.3	3.1
1D	1.78	1.12	69.64	29.85	0.51		180	18.7	39.0	0.9
1E	2.66	1.68	69.64	29.85	0.51		160	19.9	39.0	0.9
1F	0.89	0.56	74.50	25.0	0.50		200	19.0	42.9	5.8
1G	1.78	1.12	74.50	25.0	0.50		200	19.9	39.8	0.5
35	1H	0.89	69.5	5.0	25.0	0.50	200	17.8	44.5	0.5
1I	0.89	0.56	64.5	10.0	25.0	0.50	160	17.9	45.0	0.0
1J	0.89	0.56	49.5	25.0	25.0	0.50	140	18.0	46.0	0.0

EGDM is ethylene glycol dimethacrylate, MMA methyl methacrylate, ST styrene,

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MAA methacrylic acid

Table 1 illustrates that styrene incorporation into the monomer mixture 2 almost completely eliminates the coagulate formation.

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Example 2

Preparation of Core-Shell Particles Containing Voids. The Shell is Polystyrene.

- 10 The process is carried out in 500 ml flask equipped with stirrer, reflux condenser, inlet for nitrogen and necks for the feed of components. The feed is fulfilled with syringe pumps.

Stage B. Polystyrene shell preparation

15 Recipe:

Latex of the core polymer prepared according to one of the embodiments of example 1

5.73 g of solid polymer

ST 93.89 g

PP (1.47 wt-% aqueous solution) 33.90 g

20 Distilled water 70.6 g

Aqueous phase for feed:

PP 0.73 g

SDBS 0.497 g

25 Distilled water 42.29 g

Latex of core-shell polymer and distilled water are charged into the flask. The flask content is heated in the nitrogen flow up to 85°C, then aqueous solution of PP is added followed by feeding styrene and aqueous phase via syringe pumps. Feeding is carried out for 130 min.

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Stage C. Neutralization and swelling of the core-shell particles.

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Recipe:

Core-shell polymer latex prepared at stage B

Ammonia aqueous solution (conc. 10.4% wt.) 4.76 g

ST 9.39 g

5 2,2,6,6 - tetramethyl-4-oxo-piperidin-oxyl-1 (TEMPO) 0.177 g

Disponil APE 257* aqueous solution (conc. 18.1% wt.) 5.32 g

* C12-14 fatty alcohol ethoxylates (degree of ethoxylation is 30)

- 10 All components (nonionic surfactant, ammonia and styrene with dissolved TEMPO) sequentially are charged into the latex dropwise within 4-5 min. Then the reflux condenser is closed and within the next 10-15 min. the temperature is increased up to 95-96°C and the reaction mixture is maintained for 60 min. Then the temperature is reduced to 85°C within 10-15 min.

15

Stage D. Polymerization of styrene added at stage C.

0.70 g of ammonia persulphate (AP) dissolved in 12.0 g of water is charged and the reaction mixture is kept at 85°C for 40 min. Then the latex is cooled and filtered.

- 20 The final diluted latex was examined by an electron microscope. A single void can be observed inside of each particle.

On the basis of core-shell particles containing voids and above mentioned film forming latex an aqueous latex blend of the following composition was prepared (weight parts):

core-shell particles containing voids 3.0

- 25 film forming polymer 7.0

water 23.3

This latex blend was used for coatings preparation and evaluation of opacifying ability (R) and gloss.

The properties of the polymer dispersions containing core-shell particles and the coatings

- 30 depending on the kind of the core polymer and presence or absence of monomer and inhibitor at stage C are listed in table 2.

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Table 2. Properties of core-shell polymer particles dispersions and the coatings

Examp- le No	Core polymer	Inhi- bitor	Monomer at stage C	Solids, wt-%	Particle size, nm	pH	Surface tension, mN/m	R	Gloss, %
2A	Ex. 1H	TEMPO	ST	31.2	840	6.6	39.8	0.91	40
2B	Ex. 1A	TEMPO	ST	32.8	870	6.4	39.9	0.94	8.5
2C	Ex. 1H	no	ST	32.8	600	7.1	39.6	0.77	47
2D	Ex. 1A	no	no	30.2	640	7.0	41.0	0.73	
2E	Ex. 1A	no	ST	31.0	660	6.4	39.0	0.80	

- Table 2 illustrates that excluding both monomer and inhibitor at neutralization stage deteriorates opacifying ability of core-shell particles containing voids significantly (examples 2C, 2D and 2E). Besides a composition of the core polymer is a very important factor providing a gloss control of the coatings prepared. When the core polymer contains ST units the coatings are glossy (example 2A and 2C). When the core polymer is free of ST units the coatings are mat (examples 2B, 2D and 2E).

Example 3

- Preparation of Core-Shell Particles Containing Voids. The Shell is MMA-MAA Copolymer.

Generally the procedure of Example 2 is used to prepare core-shell particles. However a recipe is distinguished and benzoquinone is used instead of TEMPO.

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Stage B. MMA-MAA copolymer shell preparation.

Latex of the core polymer prepared

according to example 1A 24.89 g

35 MMA 24.28 g

MAA 0.49 g

PP 0.19 g

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Distilled water 128.0 g

Aqueous phase for feed:

PP 0.27 g

5 SDBS 0.13 g

Distilled water 15.3 g

A feeding of MMA and aqueous phase is carried out for 102 min.

10 Stage C. Neutralization and swelling of the core-shell particles.

Core-shell polymer latex prepared at stage B.

Ammonia aqueous solution (conc. 12.4% wt.) 3.2 g

MMA 1.27 g

15 MAA 0.026 g

Benzoquinone 0.07 g

Disponil APE 257 aqueous solution (conc. 18.1% wt.) 3.32 g

Stage D. Polymerization of MMA and MAA added at stage C.

20

Neutralized latex at stage C

AP 0.20 g

Distilled water 2.0 g

The final diluted latex was examined with an electron microscope. A single void can be
25 observed inside of each particle. The procedure of the coating preparation is the same as in
example 2.

The properties of the polymer dispersions and the coatings are listed in table 3.

30 Table 3

Example No	Inhibitor	Solids; % wt.	Particle size, nm	pH	Surface tension, mN/m	R	Gloss. %
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3A	Benzoquinone	32.0	820	6.9	42.4	0.97	8.0
3B	no	33.6	700	7.1	43.2	0.90	10.0

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Table 3 illustrates that elimination of inhibitor (example 3B) deteriorates opacifying ability. The coatings are mat due to the core polymer used (example 1A) does not contain ST units.

10

Example 4

Preparation of Core-Shell Particles Containing Voids. The Shell is double layered.

15 Generally the procedure of Example 3 is used. However a recipe is distinguished.

Recipe:

Stage B. Step 1

Latex of the core polymer prepared according to example 1A 26.36 g

20 Monomer mixture 1: MMA 10.39 g

ST 8.41 g

MAA 0.40 g

EGDM 0.23 g

PP 0.19 g. Distilled water 38.0

25

Aqueous phase for feed:

PP 0.276 g

SDBS 0.145 g

Distilled water 12.21 g

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A feeding of the monomer mixture 1 and aqueous phase is carried out for 108 min.

Stage B. Step 2.

Step 2 starts straight away after the completion of step 1.

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Latex prepared at step 1 of the following monomer mixture 2:

MMA	1.28 g
ST	11.36 g
EGDM	0.15 g

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Aqueous phase for feed:

PP	0.187 g
SDBS	0.098 g
Distilled water	8.25 g

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A feeding of the monomer mixture 2 and aqueous phase is carried out for 73 min.

Stage C. Neutralization and swelling of the core-shell particles.

Core-shell polymer latex prepared at stage B

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Ammonia aqueous solution (conc. 12.4% wt.)	3.15 g
Monomer mixture 2	3.23 g
Benzoquinone	0.06 g
Disponil APE 257 aqueous solution	3.30 g

20 (conc. 18.1%)

Stage D. Polymerization of monomer mixture 2 added at stage C.

Neutralized latex at stage C

AP	0.19 g
25 Distilled water	10.0 g

The final diluted latex was examined with an electron microscope. A single void can be observed inside of each particle. The procedure of the coating preparation is the same as in example 2.

30 The properties of the polymer dispersions and the coatings are listed in table 4.

Table 4

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Example	Inhibitor	Solids, % wt.	Particle size, nm	pH	Surface tension, mN/m	R	Gloss, %
5 4A	Benzoquinone	30.1	840	8.5	40.1	0.95	8.0
4B	no	30.0	710	8.0	38.5	0.90	12.0

Table 4 illustrates that elimination of inhibitor (example 4B) deteriorates opacifying ability. The coatings are mat due to the core polymer used (example 1A) does not contain ST units.

Example 5

15 Preparation of Core-Shell Particles Containing Voids with an Additional Crosslinked External Shell (Stage E).

Recipe:

Latex prepared according to example 4A	132.0 g
20 ST	23.17 g
EGDM	0.71 g
PP	0.19 g
Distilled water	10.0 g

25 Aqueous phase for feed:

PP	0.351 g
SDBS	0.184 g
Distilled water	15.49 g

30 The process is carried out in 250 ml flask equipped with stirrer, reflux condenser, inlet for nitrogen and necks for the feed of components. The latex and distilled water are charged into the flask and heated up to 85°C with stirring and nitrogen flow. Then PP aqueous solution is added and in 10 min. the monomer mixture and aqueous phase are simultaneously fed into the latex within 137 min. Then the process continues for another 35 30 min. followed by cooling, discharging and filtering of the latex prepared. The procedure

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of examination of the core-shells particles containing voids and the coatings prepared is the same as in example 2.

The properties of the polymer dispersion and the coatings are as follows:

5 Solids 35.0% wt.
PH 8.0
Particle size 950 nm
Surface tension 63.0 dyne/cm
R 0.93
10 Gloss 11 %

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Claims

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1. A process for making core-shell polymer particles containing voids comprising (A) emulsion polymerization of a core from a core monomer system comprised of at least one unsaturated monomer containing acid functionality optionally in the presence of seed latex; (B) encapsulating said core with a hard shell by emulsion polymerizing a shell monomer
10 system containing at least a vinyl aromatic or/and unsaturated carboxylic ester in the presence of said core, and (C) swelling at elevated temperature the resultant core-shell polymer particles with volatile base so as to produce an aqueous dispersion of particles which, when dried contain a microvoid which causes opacity in compositions in which they are contained, characterized in that said shell monomers, a radical inhibitor and a
15 nonionic surfactant are charged into the dispersion of said core-shell particles at stage (C) followed by (D) polymerization of shell monomers charged at stage (C).
2. The process according to claim 1 characterized in that said core monomer system consists of (meth)acrylic ester, unsaturated carboxylic acid, crosslinking monomer, and
20 optionally vinyl aromatic monomer, weight ratio of said monomers being equal to (50.0-79.9)/(20.0-40.00)/(0.1-1.0)/(0-10.0).
3. The process according to claim 1 or 2 characterized in that the volatile base is ammonia or an organic amine such as trimethyl amine, triethyl amine, diethylethanol
25 amine, or a mixture of them.
4. The process according to claim 1 to 3 characterized in that the inhibitor is benzoquinone, hydroquinone, nitrobenzene, trinitrobenzene, diphenylpicryl hydrozyl or nitroxy radical.
30
5. The process according to claim 1 to 4 characterized in that the nonionic surfactant is an ethoxylated aliphatic alcohol or phenol

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6. The process according to claim 1 to 5 characterized in that said shell monomer system comprises styrene and/or (meth)acrylic ester and optionally unsaturated carboxylic acid and crosslinking monomer.
- 5 7. The process according to claim 1 and 6 characterized in that said shell monomer system consists of two monomer mixtures polymerizing sequentially, the first monomer mixture comprising vinyl aromatic monomer, (meth)acrylic ester, unsaturated carboxylic acid and crosslinking monomer and the second one comprising vinyl aromatic monomer, (meth)acrylic ester and crosslinking monomer.
- 10 8. The process according to claim 3 or 6 characterized in that said shell monomer system comprises 1-2% by weight unsaturated carboxylic acid.
9. The process according to claims 1 to 8 characterized in that the temperature in stage
15 (C) is from 80°C to 96°C and higher than the glass transition temperature of the shell polymer at stage (C).
10. The process according to claims 1 to 9 characterized in that at least additional shell (E) is polymerized subsequent to stage (D).
- 20 11. The process according to claims 1 to 10, characterized in that stages (A) and (B) are carried out at continuous feeding of all of the components as two flows, the first one comprising the monomer mixture and the second one comprising the aqueous solution of initiator and surfactant.
- 25 12. A composition comprising core-shell polymer particles prepared according to the process of claim 1.
13. Opaque and glossy coating prepared with the composition of claim 12 comprising core-
30 shell polymer particles provided a core of said particles is produced with a core monomer system containing (meth)acrylic monomer, unsaturated carboxylic acid, crosslinking monomer and vinyl aromatic monomer.

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14. Opaque coatings with low gloss prepared with the composition of claim 12 comprising core-shell polymer particles provided a core of said particles is produced with a core monomer system which does not contain vinyl aromatic monomer.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00371

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08J 9/20, C08F 2/22, C08F 265/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08J, C08F, B01J, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9404603 A1 (THE DOW CHEMICAL COMPANY), 3 March 1994 (03.03.94), abstract, claims	1-14
X	US 4970241 A (ALEXANDER KOWALSKI ET AL), 13 November 1990 (13.11.90), column 9, line 7 - line 30	1-14
A	EP 0451940 A2 (TIOXIDE GROUP PLC), 16 October 1991 (16.10.91), abstract, claims, examples 3-8	1-14
A	US 5639805 A (JONG MYUNG PARK ET AL), 17 June 1997 (17.06.97), column 9, line 1 - line 35, abstract, claims	1-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

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PCT/FI 00/00371

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5157084 A (DO I. LEE ET AL), 20 October 1992 (20.10.92) --	1-14
A	EP 0404184 A2 (NIPPON ZEON CO., LTD.), 27 December 1990 (27.12.90) --	1-14
A	US 4973670 A (CHARLES J. McDONALD ET AL), 27 November 1990 (27.11.90) --	1-14
A	WO 9511265 A1 (LUCKY LTD.), 27 April 1995 (27.04.95), abstract, claims --	1-14
A	US 5360827 A (HIDEKI TODA ET AL), 1 November 1994 (01.11.94), abstract, claims, examples --	1-14
A	US 4594363 A (ROBERT M. BLANKENSHIP ET AL), 10 June 1986 (10.06.86), abstract, claims --	1-14
A	WO 9839372 A1 (NESTE OY), 11 Sept 1998 (11.09.98), abstract, examples, claims --	1-14
A	WO 9855522 A1 (NESTE OY), 10 December 1998 (10.12.98), examples, claims --	1-14
P,X	EP 0959176 A1 (ROHM AND HAAS COMPANY), 24 November 1999 (24.11.99), abstract, claims, examples 1-4 -- -----	1-14

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

08/05/00

International application No.

PCT/FI 00/00371

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9404603 A1	03/03/94	AU 666332 B AU 2506692 A BR 9207160 A CA 2140035 A EP 0656033 A,B SE 0656033 T3 FI 950733 A JP 8500621 T US 5521253 A BR 1101170 A DE 69219904 D,T	08/02/96 15/03/94 31/10/95 03/03/94 07/06/95 17/02/95 23/01/96 28/05/96 14/03/00 11/12/97
US 4970241 A	13/11/90	AT 91491 T AU 616756 B AU 3486889 A BR 8902330 A CA 1303438 A CN 1032013 B CN 1040039 A DE 68907521 D,T DK 244989 A EP 0342944 A,B SE 0342944 T3 ES 2058519 T FI 93017 B,C FI 892446 A HK 123093 A IE 64597 B IL 90355 A JP 2064103 A JP 2774145 B KR 158367 B MX 164012 B NO 173391 C NO 891978 D NZ 229145 A PH 25322 A SG 103593 G US 4880842 A	15/07/93 07/11/91 23/11/89 09/01/90 16/06/92 12/06/96 28/02/90 02/12/93 21/11/89 23/11/89 01/11/94 31/10/94 21/11/89 19/11/93 23/08/95 01/12/92 05/03/90 09/07/98 15/01/99 09/07/92 08/12/93 00/00/00 23/12/91 30/04/91 21/01/94 14/11/89

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INTERNATIONAL SEARCH REPORT

Information on patent family members

08/05/00

International application No.

PCT/FI 00/00371

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0451940 A2	16/10/91	SE 0451940 T3 AU 636456 B AU 7261391 A CA 2038258 A DE 69115546 D,T DK 451940 T ES 2080888 T FI 99231 B,C FI 911544 A GB 2242437 A,B JP 4224803 A US 5229209 A ZA 9101604 A	29/04/93 03/10/91 01/10/91 02/05/96 29/01/96 16/02/96 31/07/97 01/10/91 02/10/91 14/08/92 20/07/93 24/12/91
US 5639805 A	17/06/97	JP 7196747 A KR 9407353 B	01/08/95 16/08/94
US 5157084 A	20/10/92	US 5521253 A	28/05/96
EP 0404184 A2	27/12/90	DE 69021947 D,T FI 100334 B FI 903109 D JP 2067919 C JP 3026724 A JP 7091390 B US 5077320 A	15/02/96 00/00/00 00/00/00 10/07/96 05/02/91 04/10/95 31/12/91
US 4973670 A	27/11/90	AU 629054 B AU 6456690 A CA 2025633 A EP 0478829 A,B SE 0478829 T3 JP 4154811 A	24/09/92 11/06/92 19/03/92 08/04/92 27/05/92
WO 9511265 A1	27/04/95	DE 69403436 D,T EP 0674673 A,B JP 2614707 B JP 7509755 T KR 177182 B US 5618888 A	05/02/98 04/10/95 28/05/97 26/10/95 15/05/99 08/04/97
US 5360827 A	01/11/94	JP 2713081 B JP 6248012 A JP 2679523 B JP 5279409 A	16/02/98 06/09/94 19/11/97 26/10/93

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